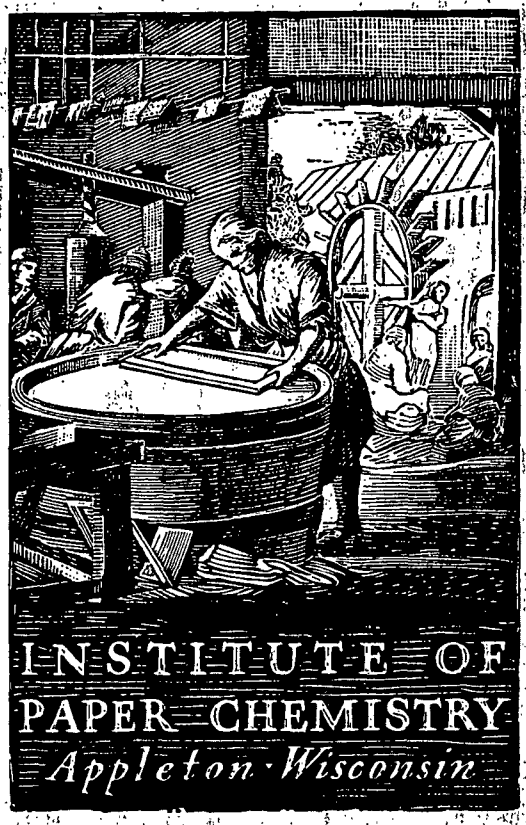

MOLECULAR STRUCTURES OF LIGNOSULFONATES

MECHANICAL AND ADHESIONAL BEHAVIOR

Project 2421

Report Fourteen

A Progress Report

to

ENVIRONMENTAL RESEARCH GROUP

June 21, 1971

THE INSTITUTE OF PAPER CHEMISTRY

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MOLECULAR STRUCTURES OF LIGNOSULFONATES MECHANICAL AND ADHESIONAL BEHAVIOR

SUMMARY

The focus of Project 2421 has been on the adhesional and mechanical behavior of lignosulfonate adhesives, and their relationship to adhesive bonding strength, particularly in plywood operations. These behavioral properties were found to be similar to good plywood adhesives and they thus have good potential. The low cohesive strength has been found to be a major limitation in lignosulfonate adhesives and this can be improved by implementing cross-linking reactions. Using water insolubility as a measure of cross-linking, the reaction of lignosulfonic acid with Catalin (an acid-sensitive, phenol-formaldehyde resin) was studied as a function of concentration, curing temperature, and time with the goal of optimizing this reasonably successful plywood adhesive. Reported herein are the results of applying the optimized conditions to the bonding of southern pine veneer and the results of examining other cross-linking reactions.

Plywood layups were made using conditions selected from the insolubility results, and were tested using the exterior grade, water boil-wet tensile test. The Holderby, et al. formulation was the best with either the ELSA or the acidified Ca spent sulfite liquor. The expected improvements as based on the insolubility data did not materialize because of combinations of overpenetration, underpenetration, and low water insolubility. The first two factors are controlled primarily by viscosity. The development of water insolubility is quite sensitive to the actual temperature history of the adhesive during the cure. The unexpected adhesive loss during the boil test of the plywood and the lack of expected bonding improvement by increased temperature alone, strongly suggest that the adhesive in

the plywood does not achieve the same temperature history as the adhesive in the glass fiber mats, due to differences in pressure buildup.

All of the adhesives pulled reasonably high quantities of wood, even those that failed seriously in the boiling step and those that penetrated very little. In the latter case it appeared to be a top layer of fibers pulled from the surface, particularly in the springwood region. This observation, coupled with the low wet bond strength (5-206 p.s.i.) of the best system compared to recent data on southern pine plywood studies (150-300 p.s.i.), suggests that the high acid conditions may be weakening the interfacial wood region.

As a circumvention for the use of Catalin, the reactions of ELSA with trioxane, or paraformaldehyde (both are formaldehyde sources) and in combination with resorcinol or phloroglucinol were explored in the above range of temperature and time. The systems in general were not as reactive as Catalin, however, at the high temperature (345°F.) and long time (6 min.) 79% insolubility was achieved with a phloroglucinol and trioxane system. Subsequently, paraformaldehyde was found to be more reactive than trioxane.

Spent sulfite liquor (CaSSL) reactions with the diepoxides, 1,2,3,4 diepoxide butane, 1,2,7,8 diepoxide octane, and Epon 812 (Shell Chemical Co.) were explored at pH 8 and pH 12, at concentrations equivalent to mole ratios of diepoxide to phenol hydroxyl of 1:2 and of 10:2, and over 275-345°F. and 4-6 min. The higher pH and higher mole ratio produce the greater insolubility. All three diepoxides at high concentration and pH set up to gels at room temperature, with the butane diepoxide reacting so fast that there was not enough time to proceed with the curing operations. The insolubility results were somewhat erratic, perhaps because most systems were two phases at the higher concentrations. An

insolubility limit of about 40 to 50% was obtained at the higher temperature (345°F.) and longer time (6 min.) for diepoxy octane and for Epon 812 at both pH's and concentrations (except as limited by the rapid gel formation).

Future work includes steps to optimize the plywood bonding by the Catalin system with respect to the actual curing temperature and adhesive viscosity. It will establish the significance of the acid condition on bonding strength by appropriate bond strength comparisons of the best lignosulfonate-Catalin system with a commercial phenol-formaldehyde adhesive on the same southern pinewood source. If the optimization progresses far enough, steps for commercial testing will be recommended.

In addition, the phloroglucinol-paraformaldehyde system will be surveyed for optimum conditions for insolubility and plywood tests will be made. Also, the very reactive diepoxide systems will be explored further. Work on both of these systems will be carried out in close cooperation with the work in the Effluent Processes Group.

INTRODUCTION

This is Progress Report Fourteen of Project 2421 entitled: "Investigation of the Relationship Between Lignin Structure and its Mechanical and Adhesional Behavior." The relationship of these properties to lignosulfonate adhesive bonding strength, particularly in plywood operations, has been investigated. The surface tension and viscomechanical behavior of these adhesives was found to be similar to that of phenol-formaldehyde resin, a good plywood adhesive. The lignosulfonate adhesives suffered from low cohesive strength which can be improved by implementing cross-linking reactions during the adhesive cure. The cross-linking effected was evaluated by the degree of water insolubility which was observed to be a direct function of plywood bond strength (1). The lignosulfonate (pH <1) – Catalin system, which has shown favorable plywood bonding (2), was examined to find the optimum conditions for maximum water insolubility (3).

The plywood bonding achieved with adhesive conditions selected from the water insolubility study are herein reported. The water insolubility results of selected phenol-formaldehyde type and epoxy type cross-linking reactions are also reported. Finally, some observations on the application of selected lignosulfonate adhesives to wood particle board and to sand binding are given.

EXPERIMENTAL

PLYWOOD LAYUPS

The plywood layups (6 x 6 in.) were made as described previously (4). The adhesive was made up in the same weight ratios of LSA and Catalin to wood flour as used by Holderby, et al. (2) which is 1:0.36. Using selected southern pine veneer which had been sanded and aged more than two weeks at 73°F. and 50% R.H., exactly four grams of adhesive were applied to each side of the center lamina of a three-ply layup. Two layups were used in each press and from six to eight layups were made with each adhesive.

PLYWOOD TESTING

Ten 1 x 3-inch specimens were cut and kerfed from each layup as previously described (4). The boil and wet tensile test for exterior-grade plywood (5) was used on all of the specimens for some layups and on every other specimen for the other layups. The remaining specimens were tensile tested without boiling. The identified specimens were placed in a twelve-liter round-bottom flask fashioned with a water overflow [the same vessel used in the water solubility measurements (1)] and boiled by steam input for the four hours. Those that remained intact were dried overnight at 125°C., were reboiled the next day, and tensile tested in the wet state using an Amsler Tester. The failure zone of each specimen was visually examined for failure point (interface or cohesive), extent of adhesive penetration, amount of adhesive left at the interface, and the amount of wood pulled in failure.

CATALIN SYSTEM

The adhesive systems made with Catalin (50% by weight in aqueous solution, designated CR-9357 by Ashland Chemical Co., Resins and Plastics Division,

Chicago), an acid-catalyzed phenol-formaldehyde resin, were prepared by adding the desired amount of Catalin based on the LSA to the LSA solution and adding any additional water to give the desired concentration of LSA. If the LSA solution was too dilute initially, a quantity of it was freeze dried and redissolved to the desired concentration.

FORMALDEHYDE AND PHENOL-FORMALDEHYDE SYSTEM

The formaldehyde source used was primarily the cyclic trimer, trioxane, although the linear polymer, paraformaldehyde, was used in a late check as it is more easily hydrolyzed and may be the better reactor. Formaldehyde was not used directly because of the odor problem. The sources were added directly to the ELSA solution (42% solids, pH = 0.45) in the concentrations arbitrarily chosen at two levels, 1 and 30% based on the ELSA.

The prepared solution was tested for cross-linking reactivity by the water insolubility measurement of the cured adhesive in a glass fiber mat, as previously described (1). Two levels of curing temperature and time were chosen, 275 and 345°F., and 4 and 6 min.

The phenol-formaldehyde system was prepared by adding sufficient mass of the phenol and the formaldehyde (trioxane determined as formaldehyde) to the ELSA to give 40% solids based on the ELSA content and mole ratios of 1:1 and 1:3 phenol to formaldehyde. The phenols tested were resorcinol and phloroglucinol. Runs were also made at 57.1% solids and 1:3 mole ratio, a condition resulting by keeping the solids concentration of phenol for the 40% — 1:1 system constant and tripling the formaldehyde content.

DIEPOXIDE SYSTEM

The diepoxide systems were prepared by adding a mass of diepoxide to the lignosulfonate solution equivalent to a one to two molar ratio of diepoxide to free phenol assuming a 1% free phenol content of the lignosulfonate (1). A concentration was also prepared making this molar ratio ten to two. The diepoxides tested were 1,2,3,4 diepoxybutane, 1,2,7,8 diepoxyoctane and Epon 812 (Shell Chemical Company). Two conditions of pH, temperature, and time were employed: pH 8 and 12, 275 and 345°F., and 4 and 6 min. The water insolubility of the cured system was determined via the glass fiber mat procedure (1).

PARTICLE BOARD PREPARATION

The desired weight of adhesive (45% ELSA, 5% Catalin) was blended with wood shavings (principally oak with small percentages of birch and maple). A quantity of this blend was placed in a 6 x 6 x 1/4 inch form (galvanized steel base with a 1/4-inch fiberboard cutout) which was lined with silicon-treated aluminum foil which was then lapped back to cover the blend. The form was then placed on the heated platens (345°F.), 200 p.s.i. pressure was applied and held for 6 min. The quantity was sufficient to give approximately 1/4-inch thickness when under the curing pressure. Wood-to-adhesive ratios of 1:1 (steam explosion), 3:1, 7:1, 15:1, 31:1, 63:1, and no adhesive were made.

BONDING SAND

The same form used in particle board preparations was employed with a sand "layup." An ungraded sand was mixed with a 45% ELSA – 5% Catalin adhesive in the weight ratio of 9:1. A quantity of this mix sufficient to give 6 x 6 x 1/4 inch was placed in the form lined with the silicon-treated aluminum foil which was folded back over the mix. The form was placed on the heated platens (345°F.), a

pressure of 200 p.s.i. was applied, and the system cured for 6 min. When cooled, a piece of the cast sand was chipped off and placed in boiling water. It disintegrated almost immediately with the water becoming very colored.

In another series of sand bonding tests, the sand was mixed with 2% by weight of adhesive and blended. The adhesive was calcium-base spent sulfite liquor (CaSSL) — 48% solids, 88% (based on CaSSL) Epon 812 adjusted to pH 12 with NaOH. Aluminum weighing dishes were filled with the sand mix and pairs of dishes were allowed to stand for 1, 3, and 7 days at room temperature and at 125°F. At the end of this period, the dishes were weighed, immersed in boiling water for 30 min., removed, dried overnight at 73°F. and 50% R.H., and reweighed. Two samples of mix were packed into 1 1/2-inch diameter paper core rolls to the depth of 1 1/2 inches. These were allowed to cure at room conditions for several weeks. The paper form was removed. The sand cores were placed on end in about 1/2 inch depth of water and the time for the core to slake was measured.

RESULTS AND DISCUSSION

PLYWOOD STUDIES

Southern pine plywood layups were prepared using conditions selected from the insolubility studies (3). Specimens from the layups were subjected to the boiling test for exterior-grade plywood (5) and in some cases directly to dry tensile test. The adhesive conditions and the results are listed in Table I The conditions selected achieved high insolubility by virtue of high concentration (LSA and/or Catalin), high temperature, and/or long time. Each of these variables was examined.

The reference point is the Holderby, et al. (2) formulation, No. 12, which was previously reported (3). The replacement of ELSA with CaSSL at low pH, No. 14, is almost comparable to No. 12 in boil survival and wet tensile, as the insolubility data indicate it should be. However, increasing the cure temperature of the Holderby adhesive from 300 to 345°F., No. 13, does not improve the wet tensile, as the solubility data would predict. Also, increasing the ELSA concentration of the Holderby adhesive even at the higher temperature, No. 3, does not improve the bonding, as the insolubility would suggest. The slightly poorer survival and wet tensile of No. 3 compared to No. 12 may be due to the very viscous nature of the former which was pasty and had to be spread on the veneer with a knife. Thus, the penetration of this adhesive was very limited which may be the cause of the wood failure in these specimens being limited to the pulling of interfacial fibers from the springwood areas. This may be a penetration limiting failure or an interfacial weakening of the wood by the high acid condition. When the wood meal is omitted from this (No. 3) adhesive, No. 4, the adhesive is more fluid and it can be applied by the usual brushing technique.

TABLE I

PLYWOOD BONDING RESULTS

No.	Adhesive	Cure °F.	Cure Min.	Insolubility in Glass Mat (3), wt. %	Wet Test Survival Number	Wet Test Tensile, lb./sq.in. Max.	Wet Test Tensile, lb./sq.in. Min.	Wet Test Tensile, lb./sq.in. Av.	Wet Test % Wood Pulled	pH	Dry Test Survival Number	Dry Test Tensile, lb./sq.in. Max.	Dry Test Tensile, lb./sq.in. Min.	Dry Test Tensile, lb./sq.in. Av.	Dry Test % Wood Pulled
1	45% ELSA, 50% Catalin	345	6	95	35/60	100	2	21 ± 13	30	0.62					
2	45%,ELSA, 50% Catalin at same ELSA solids as Holderby formulation	345	6	95	46/60	74	4	30 ± 13	40	0.62					
3	45% ELSA, 40% Catalin	345	4	92	54/60	219	3	35 ± 12	50	0.40					
4	45% ELSA, 40% Catalin, no wood meal	345	6	93	31/40	63	3	17 ± 6	15	0.40	38/40	450	62	189 ± 36	45
5	45% CaSSL, 10% Catalin	345	5	--	14/60	31	3	10 ± 4	30						
6	45% CaSSL, 10% Catalin and 2% Polyox	345	5	--	2/40	10	9	10 ± 1	40		40/40	368	36	113 ± 35	40
7	45% CaSSL, 10% Catalin heated before wood meal added to increase viscosity	345	5	--	0/5			--			5/5	118	57	83 ± 20	45
8	45% CaSSL, 10% Catalin aged at room temp. to increase viscosity	345	5	--	0/40			--			39/40	315	22	89 ± 20	35
9	45% ELSA, 5% Catalin	345	5	80	2/60	71	19	45 ± 37	10	0.54					
10	45% ELSA, 5% Catalin, 4 g. each surface	345	5	80	1/30	--	--	6		0.54	28/30	201	47	95 ± 27	40
11	45% CaSSL, 5% Catalin	345	5	(55)	2/60	12	6	9 ± 4	40						
12	30% ELSA, 40% Catalin	300	4	64	60/60	206	5	84 ± 20	55	(0.9)	95/100	358	102	212 ± 23	
13	30% ELSA, 40% Catalin	345	4	87	60/60	161	3	55 ± 22	50						
14	30% ELSA, 40% Catalin, ray cells instead of wood meal	345	6	90	0/40			--			40/40	200	5	68 ± 23	5
15	30% CaSSL, 40% Catalin	300	4	(70)	59/60	196	4	66 ± 14	40	(0.3)					
16	30% CaSSL, 40% Catalin, pH = 3.0	345	5	(52)	0/40			--			20/40	260	4	74 ± 50	0

The penetration is improved over No. 3 but there is also a noticeable loss of solid adhesive at the interface after the boil test, suggesting lower insolubility than anticipated, particularly when compared to the adhesive with wood meal (No. 3). This may account for the lower survival, wet tensile, and wood pull of No. 4 compared to No. 3 while its dry tensile approaches that of the Holderby reference, No. 12. The lower insolubility may be caused by a lower temperature-time history due to a slower pressure-temperature buildup in the absence of a fine-pore-wood-meal matrix. The layup with the optimum insolubility adhesive, No. 1, and its application at the same ELSA solids to the glue line as Holderby work, No. 2 were about comparable to No. 3 both in viscosity (pasty) and performance. Again, the limited penetration may have reduced their performance compared to the Holderby reference, No. 12.

Layups with the high insolubility — low Catalin, No. 9, showed surprisingly poor bonding behavior, both wet and dry, compared to the Holderby reference No. 12. There was extensive penetration, particularly into the springwood and the bond failure was primarily summerwood-adhesive interfacial failure. The wood pulled was primarily springwood, as was the case in essentially all of the plywood layups in this study. The low dry tensile suggests overpenetration weakening but there is also evidence of low adhesive insolubility based on a visual comparison of No. 9 with No. 3. Doubling the glue mass by also coating the outer veneer face did not improve the wet bond performance and the dry tensile was quite low compared to No. 12. This low Catalin content adhesive is quite sensitive to the platen temperature (3), thus a lower temperature-time history than achieved in the insolubility study would be quite detrimental to cross-linking, causing lower insolubility and cohesive strength. The use of CaSSL with the same 5% Catalin adhesive, No. 11, gives comparable results with the ELSA adhesive, No. 9.

Increasing the Catalin to 10%, No. 5, improves the wet survival some but not the bonding strength and the system still suffers from overpenetration and what appears to be low insolubility. To reduce the penetration, the viscosity was increased by application of a little heat, No. 7, but the reaction was too fast and only one layup could be made before the adhesive became too thick. By letting the adhesive age at room temperature, the viscosity increase was easier to control and a six-hour period gave a reasonably handling adhesive, No. 8. The wet survival of No. 7 and No. 8 was zero and yet there appeared to be reasonable penetration into the springwood. However, their low dry tensiles compared to No. 12 suggest low cohesive strength which probably results from a lower temperature-time history, as previously discussed. The addition of Polyox WSR-301 (Union Carbide Corp.), a polyethylene oxide, to the adhesive for improvement of the adhesive flexibility was tried in layups No. 6. The survival decreased some compared to No. 5 but the dry tensile increased some, suggesting an increase in adhesive flexibility; however the effect is small and No. 6 is still very much weaker than No. 12.

When the wood meal of the Holderby formulation is replaced with ray cell solids (the precipitate in the ultrafiltration rejects of spent sulfite liquor processing which contain a high portion of xylans, probably as ray cells) the layups No. 14 have very poor wet survival. The wet specimens show no evidence of adhesive remaining. The low water insolubility indicates a low cohesive strength which is reflected in the low dry tensile.

In summary, the promising adhesives based on insolubility results have produced plywood bonding which is about equal to or poorer than that of the Holderby formulation. One cause of this bonding weakness may be due to a lower temperature-time history of the adhesive on the porous wood substrate compared to that on the aluminum enveloped glass fiber mat substrate, causing lower water

insolubility and cohesive strength than expected. Along with this are possibilities of adhesive loss from the interface by overpenetration, or of poor mechanical linkage from underpenetration of the adhesive, depending on the adhesive viscosity. Finally, there is a possibility of a weakening of the adhesive wood interface because of the high acid conditions of the adhesive. With regard to this last possibility, it is significant to note that the range of wet tensiles for the best bonded system studied here (No. 12) is 5-206 p.s.i., whereas the range reported recently by Hse (6) with basic phenol-formaldehyde adhesives also on southern pine is 150-300 p.s.i.

Since low pH might be a contributing factor to plywood bonding weakness, the effect of increasing the pH on the water insolubility of a cured CaSSL-Catalin system was studied by the glass fiber mat method (1). The results are listed in Table II. (See Appendix I for the basic data.) As the pH increases, the insolubility decreases for a given temperature and time. However, at the highest temperature and longest time (345°F.-6 min.) 56% insolubility was achieved at the highest pH = 3.0, which is almost as good as the Holderby adhesive as used at 300°F. and 4 min. However, layups prepared at this high pH and maximum cure conditions (No. 16 in Table I) gave very poor wet behavior and very weak dry tensile. The adhesive suffered both from high penetration and low water insolubility as a result of low viscosity and probably a low temperature-time history, as previously discussed.

In addition to pH, the effects of hardwood lignosulfonates, of Polyox, of increased molecular weight, and of CaSSL with low Catalin on water insolubility as determined by the glass fiber mat system were examined. The results are listed in Table II. The hardwood is significantly less reactive with Catalin than the softwood lignosulfonates used in the other studies. This result is consistent with the higher syringyl-to-guaiacyl ratio of the former since the phenol-formaldehyde

TABLE II

WATER INSOLUBILITY OF CURED ADHESIVE[a] AS A FUNCTION OF pH AND OTHER FACTORS

		CaSSL					ELSA	CaSSL	ELSA		CaSSL	ELSA
pH		3.0	2.5	2.0	1.5	0.2	0.45	Hardwood 0.3	2% Polyox 1.0	Refluxed 1.5	45%-5% 1.0	45%-5% 0.54
Temp., °F.	Time, min.											
275	4	-39	23	28	33	63	58	15	70	63	6	-26
	6	35	38	43	40	72	54	25	82	78	22	26
345	4	49	45	65	66	79	87	37	90	86	57	75
	6	56	56	67	62	90	90	43	91	95	54	83
	viscy.[b], sec.	4.4	4.8	5.2	5.5	--		3.1	stringy	6.8	10.5	
							(13 cp.)			(~48 cp.)		(300 cp.)

[a]The lignosulfonate-Catalin concentrations are 30%-40% unless otherwise indicated.

[b]This relative viscosity is the time required to drain a given 10 ml. graduated pipet. Some corresponding drainage times and viscosities are: 2.8 sec. = 1.0 cp., 4.4 sec. = 18 cp., and 7.7 sec. = 60 cp. The viscosity of the ELSA refluxed adhesive was interpolated from these data.

condensations require an open ortho or para position with respect to the phenolic hydroxyl. The presence of Polyox has little effect on the insolubility reaction. An increase in molecular weight (a molecular weight change producing over a three-fold increase in viscosity) does not have much effect on the insolubility reaction. Finally, the CaSSL does not appear to be as reactive as ELSA at 45% concentration with 5% Catalin, which may account for some of the poor plywood bonding of layups No. 5-8 and 11.

OTHER CROSS-LINKING REACTIONS

As a possibility of implementing phenol-formaldehyde-type reactions during the adhesive cure, insolubilities were determined for ELSA with trioxane (a nonodorous source of formaldehyde) at concentrations of 1 and 30% with respect to ELSA, and with resorcinol or phloroglucinol and trioxane at mole ratios of 1:1 and 1:3. The latter mole ratio represents the maximum molecular coupling possible with these phenolic molecules. The results are given in Table III. (See Appendix I for the basic data.) Neither trioxane nor trioxane with resorcinol is reactive enough under the temperature and time conditions used to give reasonable levels of insolubility. However, phloroglucinol with trioxane in mole ratio 1:3 does give reasonably high levels of insolubility (73-79%) at the high temperature and, for the most part, longer time. Since paraformaldehyde (a low odor source of formaldehyde) is more easily hydrolyzed than trioxane, the insolubility reaction was determined with this agent at 30% and found to be moderately successful. The reactions of ELSA with combinations of paraformaldehyde and phloroglucinol and perhaps even with resorcinol should be explored.

Cross-linking reactions of spent sulfite liquors with diepoxide under alkaline conditions were also examined for the development of water insolubility.

TABLE III

WATER INSOLUBILITY OF CURED ADHESIVES MADE FROM ELSA (42% SOLIDS, pH = 0.45) WITH FORMALDEHYDE SOURCES AND WITH PHENOLS

Temp., °F.	Time, min.	Trioxane 30%[b]	Paraform-aldehyde 30%	Resorcinol Trioxane 40% 1:1	Phloroglucinol Trioxane 40% 1:1
275	4	--	-20	--	--
	6	--	18	--	--
345	4	-26	31	--	-32
	6	--	31	--	59
	pH	0.5	--	0.45	0.50
	viscy.[a], sec.	5.0	--	5.3	6.2
		1%		40% 1:3	40% 1:3
275	4	--		--	--
	6	--		--	--
345	4	--		--	79
	6	--		-16	77
	pH	0.50		0.40	0.55
	viscy.[a], sec.	6.0		5.0	5.8
				57.1% 1:3	57.1% 1:3
275	4			--	--
	6			--	--
345	4			--	7
	6			10	73
	pH			0.80	0.90
	viscy.[a], sec.			5.0	5.8

[a] This relative viscosity is the time to drain the contents from a given 10 ml. graduated pipet.

[b] The concentrations are with respect to the ELSA solids. When appropriate the ratio of phenol to formaldehyde is also given.

The agents tested were 1,2,3,4 diepoxybutane, 1,2,7,8 diepoxyoctane, and Epon 812 (Shell Chemical Co.) at pH 8 and 12 and concentrations equivalent to 1:2 and 10:2 mole ratios of agent to phenolic hydroxyl, assuming 1% by wt. of phenolic hydroxyl content in the SSL (1). The results are listed in Table IV. (See Appendix I for the basic data.) The higher pH and higher mole ratio produce the greater insolubility. All three diepoxides at high concentration and pH set up to gels at room temperature. The diepoxybutane reacted so fast that there was not enough time to proceed with the curing operations. The insolubility results were somewhat erratic, perhaps because most systems were two phases at the higher concentrations. An insolubility limit of about 40 to 50% was obtained at the high temperature (345°F.) and long time (6 min.) for diepoxyoctane and for Epon 812 at both pH's and concentrations (except as limited by the rapid gel formation). Considering the amount of alkali added to reach the desired pH and the unreacted diepoxide remaining, particularly at the high concentration, this insolubility limit may represent most of the SSL material originally present. Epon alone at about the same concentration and viscosity (increased by the addition of a small amount of Polyox) gave less than 10% insoluble products under the same conditions. The high reactivity of these diepoxides makes them worthy of further work.

APPLICATIONS

Samples of particle board 6 x 6 x 1/4 inch were made using wood shavings and 45% ELSA – 5% Catalin cured at 345°F. for 6 min. The boards produced with varying amounts of adhesive were structurally coherent but other tests were not made on them.

A coarse sand matrix 6 x 6 x 1/4 inch was made with 10% adhesive of 45% ELSA – 5% Catalin cured at 345°F. and 6 min. The cured matrix was coherent

TABLE IV

WATER INSOLUBILITY OF CURED ADHESIVES MADE WITH LIGNOSULFONATES AND DIEPOXIDE UNDER ALKALINE CONDITIONS

		NH_4SSL (51% Solids, pH = 3.0)				CaSSL (48% Solids, pH = 0.2)	
		1,2,3,4 Diepoxybutane 25%[c]		1,2,7,8 Diepoxyoctane 41%		Epon 812 88%	
Temp., °F.	Time, min.	pH = 8	pH = 12	pH = 8	pH = 12	pH = 8	pH = 12
				two phase		two phase	
275	4	--		13	--	--	47
	6	12		14	--	-33	49
345	4	--		42	--	20	54
	6	7		48	--	39	48
	NaOH[a]	20	45	20	45	16	25
	viscy.[b], sec.	22.5	gel	24.0	20.0	11.0	gel within 3 hr.
		2.5%		4.1%		8.8%	
275	4	--	--	--	--	--	22
	6	--	--	--	--	1	26
345	4	--	--	--	--	22	38
	6	--	--	--	--	45	41
	NaOH[a]	20	45	20	45	16	25
	viscy.[b], sec.	22.0	too thick	27.0	--	--	--

[a] This is the number of sodium hydroxide pellets per 50 g. of sample required to achieve the given pH. There are 1.4 g. to seven pellets.

[b] This relative viscosity is the time to drain the contents from a given 10 ml. graduated pipet.

[c] The concentration is with respect to the lignosulfonate solids.

but the adhesive from a test piece quickly dissolved in hot water. In view of the expected insolubility (>80%) the temperature-time history was probably too low to achieve the desired insolubility.

Two percent adhesive of 48% CaSSL – 88% Epon 812 at pH 12 was added to a quantity of coarse sand. Samples of this material were allowed to cure at room temperature and at 125°F. for one to seven days. In all cases, the adhesive was hot-water extractable although the extracted-dried samples had a top crust which was probably formed from the undissolved Epon 812. The slaking rate of room temperature-cured samples, 1 1/2 inch diameter x 1 1/2 inch high, was also very fast (<5 sec.). Thus, the adhesive insolubility developed was not very great in spite of the gel structure developed by the parent adhesive. A study of the reaction conditions of SSL with diepoxides may improve the insolubility results.

CONCLUSIONS

There was not a good correlation between the water insolubility behavior of the lignosulfonate-Catalin adhesive and the plywood bonding behavior. However, there are indications that the temperature-time history in the plywood system may be lower than that in the aluminum-contained glass fiber mat system used in the insolubility measurements. This history is rather crucial to successful cross-linking. In addition, viscosity variations of the adhesives led to apparent under-penetration or overpentration, depending on the viscosity extreme, and there also may be some weakening of the wood near the interface due to the high acid conditions of the adhesive.

The phenol-formaldehyde — lignosulfonic acid cross-linking reactions with the elementary reactants are possible at reasonable curing temperatures and times. The system with paraformaldehyde and phloroglucinol or perhaps resorcinol shows promise. Under alkaline conditions the spent sulfite liquors react quite readily with diepoxide cross-linking agents.

FUTURE WORK

The properties needing evaluation in the LSA-Catalin plywood adhesive are (1) curing temperature history, (2) acid degradation of wood, and (3) viscosity, in that order of significance. The curing temperature history will be recorded both in the glass fiber mat system and in the plywood. If needed, the adhesive boiling point will be raised by replacing water with glycol or by making an autoclave press. The effect of acid on the wood strength will be determined by comparing the wet tensile of the test adhesive with that of a nonacid commercial plywood adhesive on the same southern pine veneer source. If pH is a problem, the pH will be increased and the temperature and time increased sufficiently to implement cross-linking. The adhesive viscosity will be varied by allowing the adhesive to react some before use and the useful viscosity limits for adequate bonding will be established.

Work will continue on other curing reactions not requiring commercial resins. The acid condition reaction of LSA with paraformaldehyde and phloroglucinol or resorcinol will be evaluated. The alkaline condition reaction of SSL with diepoxides also will be considered further. This work will be done in close cooperation with the Effluent Processes Group.

Applications of selected adhesives will be made to particle boards and methods of testing these will be set up. The binding of road aggregate with promising adhesive will be evaluated by measurement of slaking rate.

Consideration will be given to commercial plywood test applications of feasible adhesives.

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APPENDIX I

BASIC DATA FOR WATER INSOLUBILITY MEASUREMENTS

Listed in Tables V, VI, and VII are the weights of the cured adhesive in the disk prior to the boiling water extraction for the pH and other factors, the phenol-formaldehyde system, and the diepoxide system, respectively.

TABLE V

WEIGHT (MG. PER DISK) OF THE CURED ADHESIVE[a] BEFORE THE WATER SOLUBILITY MEASUREMENT IN THE STUDY OF pH AND OTHER FACTORS. (SEE TABLE II)

		CaSSL					ELSA	CaSSL	ELSA		CaSSL	ELSA
pH		3.0	2.5	2.0	1.5	0.2	0.45	Hardwood 0.3	2% Polyox 1.0	Refluxed 1.5	45%-5% 1.0	45%-5% 0.54
Temp., °F.	Time, min.											
275	4	234.4	203.9	173.9	272.9	209.7	149.5	200.4	202.0	235.9	244.0	269.4
	6	182.5	205.1	240.5	277.2	217.8	121.6	246.3	271.2	187.9	280.1	286.6
345	4	171.6	182.7	340.9	411.6	172.0	259.5	261.2	352.5	154.5	323.1	483.4
	6	154.4	213.1	256.7	379.9	289.2	195.4	262.1	308.5	496.4	205.1	501.2

[a]The lignosulfonate-Catalin concentrations are 30%-40% unless otherwise indicated.

TABLE VI

WEIGHT (MG. PER DISK) OF THE CURED ADHESIVE BEFORE WATER SOLUBILITY MEASUREMENT IN THE STUDY OF ELSA (42% SOLIDS, pH = 0.45) WITH FORMALDEHYDE SOURCES AND WITH PHENOLS. (SEE TABLE III)

Temp., °F.	Time, min.	Trioxane 30%[a]	Paraform-aldehyde 30%	Resorcinol Trioxane 40% 1:1	Phloroglucinol Trioxane 40% 1:1
275	4	151.6	134.0	228.1	168.5
	6	153.2	189.6	191.8	195.9
345	4	220.0	154.9	197.2	169.1
	6	166.2	166.0	219.5	205.1
		1%		40% 1:3	40% 1:3
275	4	112.0		189.4	191.0
	6	160.4		143.6	185.7
345	4	162.6		156.9	195.7
	6	186.7		217.5	189.4
				57.1% 1:3	57.1% 1:3
275	4			142.0	219.1
	6			164.9	138.8
345	4			220.4	199.1
	6			239.6	183.8

[a] The concentrations are with respect to the ELSA solids. When appropriate the ratio of phenol to formaldehyde is also given.

TABLE VII

WEIGHT (MG. PER DISK) OF THE CURED ADHESIVE BEFORE THE WATER SOLUBILITY MEASUREMENT FOR THE LIGNOSULFONATE-DIEPOXIDE REACTION. (SEE TABLE IV)

		NH_4SSL (51% Solids, pH = 3.0)				CaSSL (48% Solids, pH = 0.2)	
		1,2,3,4 Diepoxybutane 25%[a]		1,2,7,8 Diepoxyoctane 41%		Epon 812 88%	
Temp., °F.	Time, min.	pH = 8	pH = 12	pH = 8	pH = 12 two phase	pH = 8	pH = 12 two phase
275	4	471.8	--	372.4	492.1	304.5	944.1
	6	713.6	--	341.6	475.0	316.2	1037.3
345	4	844.7	--	416.1	417.2	350.1	1032.9
	6	1131.5	--	410.1	Disks stick to Al.	399.2	1362.7
		2.5%		4.1%		8.8%	
275	4	320.1	466.4	429.1	571.9	290.5	392.7
	6	369.1	471.3	299.6	438.1	257.8	364.8
345	4	370.1	555.8	413.2	535.9	291.3	596.6
	6	528.8	411.1	371.9	564.8	474.6	414.3

[a]The concentration is with respect to the lignosulfonate solids.